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Conducting hydrogels for edible electrodes

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Abstract

The development of highly swollen, strong, conductive hydrogel materials is necessary for the advancement of edible device research. Using a gellan gum/gelatin ionic-covalent entanglement (ICE) hydrogel, a simple method of producing conductive, edible hydrogels is described. ICE gels containing NaCl or CsCl were developed which exhibited conductivities of 200 ± 20 mS cm^{-1} and 380 ± 30 mS cm^{-1}, respectively. Furthermore, the potential of food grade products for use as edible electrodes was examined by analysing the electrical properties of alginate-gelatin hydrogels, Vegemite, Marmite, jelly and gold leaf. Lastly, these edible ICE gels were used to demonstrate a capacitive pressure sensor from consumable materials, which displayed a sensitivity of 0.80 ± 0.06 pF kPa^{-1} for a range of 4-20 kPa. The pressure exerted by the GI tract on its contents is standardly 0.7 kPa to 6.3 kPa. This suggests potential for application in the detection of digestive pressure abnormalities such as intestinal motility disorders.

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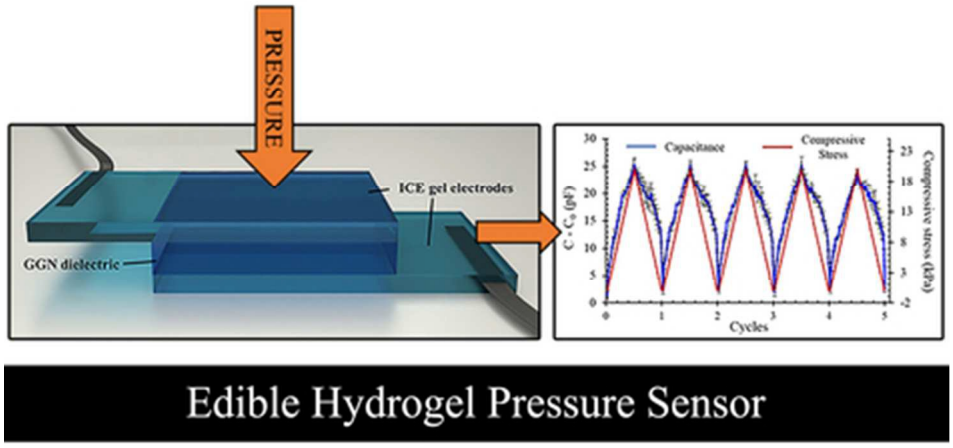

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One sentence to describe novelty of this work:

Conducting hydrogels prepared from edible, commercially available materials were shown to function as capacitive pressure sensors.

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Conducting Hydrogels for Edible Electrodes

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The development of highly swollen, strong, conductive hydrogel materials is necessary for the advancement of edible device research. Using a gellan gum/gelatin ionic-covalent entanglement (ICE) hydrogel, a simple method of producing conductive, edible hydrogels is described. ICE gels containing NaCl or CsCl were developed which exhibited conductivities of 200 ± 20 mS/cm and 380 ± 30 mS/cm, respectively. Furthermore, the potential of food grade products for use as edible electrodes was examined by analysing the electrical properties of alginate-gelatin hydrogels, Vegemite, Marmite, jelly and gold leaf. Lastly, these edible ICE gels were used to demonstrate a capacitive pressure sensor from consumable materials, which displayed a sensitivity of 0.80 ± 0.06 pF/kPa for a range of 4-20 kPa. The pressure exerted by the G.I tract on its contents is standardly 0.7 kPa to 6.3 kPa. This suggests potential for application in the detection of digestive pressure abnormalities such as intestinal motility disorders.

1. Introduction

Gastrointestinal (GI) conditions are one of the most prevalent health concerns within society. An estimated 10-15% of Americans suffer from irritable bowel syndrome (IBS)[1] and stomach cancer causes the second highest cancer related deaths.[2] However, although these illnesses are widespread, the detection of GI conditions before they become symptomatic is extremely rare; with 76.6% of people suffering from IBS going undiagnosed.[3] This is most likely a result of current methods of monitoring the GI tracts, such as endoscopy, colonoscopy and surgery, being expensive, dangerous and very invasive. Recently, a less invasive, simpler alternative has emerged known as electronic capsules.

Electronic capsules are small, transient devices which pass through the digestive system monitoring or treating the condition of the GI tract.[4–7] However, capsule retention have been shown to occur in approximately 1.9% of cases.[8] Therefore as these capsules contain toxic components, this technology cannot be used for regular GI treatment or diagnostics. To circumvent this issue of retention a field of research has emerged known as edible devices.

Edible devices/electronics or bioelectronics offer a possible solution to capsule retention as devices are constructed from edible materials which can be reabsorbed by the body.[9] This ability for devices to be digested makes them ideal candidates for regular (e.g. weekly or daily) monitoring or treatment of the GI tract. Although edible devices are a recent advent several simple constructs have been demonstrated, such as edible batteries[10,11] and an edible RFID tag.[12] The construction of edible electronics requires the use of consumable materials which can be chemically modified to withstand the harsh conditions of the GI tract and display properties useful for device development such as conduction. Hydrogels are presented as an ideal candidate to achieve these goals.

Hydrogels are materials consisting of hydrophilic polymer networks which can hold vast quantities of water. When these polymers are swollen in water they become soft and rubbery and can easily mimic the elastic modulus of biological tissue.[13] They can be manufactured to be biodegradable, biocompatible[13] and responsive to external stimuli, such as electrical or environmental changes.[14] Hydrogels are common in everyday products such as diapers[15], wound dressings[16], contact lenses[17] and many more. Most importantly for edible devices is that these materials have been widespread in food products, with common hydrogel forming polymers, such as alginate, gellan gum and gelatin being key ingredients in ice cream, yogurt and marshmallows.[18–20] Therefore, as hydrogels are cheap, abundant, elastic and digestible they are an ideal material for edible electronics. However, most hydrogels are typically mechanically weak and need to be reinforced for application in edible devices.

One method used to increase the mechanical properties of these hydrogels is to produce what is known as an interpenetrating polymer network (IPN).[21,22] IPNs are produced via the uniform mixing of two independently crosslinked polymer networks. One of the most common forms of IPNs consists of two covalently crosslinked polymer networks, which are known as double network (DN) hydrogels.[23] The incorporation of these two networks has shown to result in synergistic strengthening of the material. Ionic-covalent entanglement (ICE) hydrogels are an additional example of IPNs, consisting of entangled ionic and covalently crosslinked polymer networks.[24–29] ICE gels exhibit excellent self-recovery properties and high mechanical toughness. This is a result of sacrificial (and reversible) bonds, i.e. the ionic network unzips over a large area when under stress, dissipating the load throughout the polymer network.[26] Furthermore, it has recently been demonstrated that these ICE gel materials can be 3D printed for rapid prototyping of devices.[30] In addition to this, these materials can be made responsive to external stimuli (heat, humidity, etc.) for the creation of 4D printed devices such as temperature responsive valves.[28,30] As hydrogels inherently possess little or no electrical conductivity, methods to induce conduction need to be explored to enable their use as edible electronics.

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Conducting hydrogels have typically been produced via the addition of a secondary conducting polymer phase, such as poly(3,4-ethylenedioxythiophene) (PEDOT)[31–33] or adding conductive fillers, such as carbon nanotubes.[34] However, as electronic conductors are inhibited by the inclusion of water, these gels must be dehydrated to raise their conductivities.[31–34] Therefore, the production of hydrogels which are both highly swollen (>80% w/w water) and conductive (>100 mS/cm) have proven unsuccessful. Ionic conduction presents a possible solution to this problem, since conduction via ionic charge carriers is facilitated, rather than impeded, by the inclusion of water.

In this paper, we describe the preparation and characterisation of mechanically robust, conducting hydrogel electrodes from edible materials. Gels were produced using food grade materials and modified via the addition of ionic charge carriers by soaking in a salt solution to induce conduction. Furthermore, the conductive properties of common supermarket products Vegemite, Marmite, jelly and gold leaf were investigated. Finally, using edible ICE gels as electrodes a simple capacitive pressure sensor was constructed to demonstrate the potential of the material for edible device development.

2. Materials and Methods

2.1. Materials

2.1.1. ICE Gels. ICE gels were prepared using gelatin, (porcine, type A, Bloom number 300, molecular weight 87.5 kDa, Sigma Aldrich, USA, lot number: 119K0062) and gellan gum (low acyl, Gelzan-CM, CP Kelco, lot number: 1I1443A). 25% (w/v) genipin (Challenge Bioproducts, Taiwan) in 60% (v/v) ethanol (Ajax Finechem, Australia) and $CaCl_2.2H_2O$ (Sigma Aldrich, Australia, lot number: MKBG9652V) solutions were used to crosslink the gelatin and gellan gum respectively.

Conducting ICE gels were prepared in salts solutions of NaCl (Sigma Aldrich, Australia, lot number: MKB9892V) and CsCl (Sigma Aldrich, Australia, lot number: SLBF2545V) dissolved in Milli-Q water (resistivity, 18.2 MΩ cm).

2.1.2. Food grade robust edible electrodes. Food grade Gelatin powder (McKenzie's, Woolworths, Australia), sodium alginate powder (The Red Spoon Co., Gourmet Goldmine, Australia), $CaCl_2$ (The Red Spoon Co., Gourmet Goldmine, Australia), SAXA NaCl Salt (Table salt, naturally evaporated sea salt, Woolworths, Australia) and tap water (Wollongong, Australia) were used to make robust, conductive, edible hydrogels.

2.1.3. Food grade conducting lines. Vegemite (Fred Walker & Co) and Marmite (Sanitarium Health and Wellbeing Company) were purchased from a local Woolworth's supermarket (Australia). Jelly electrodes were prepared from commercially available aeroplane jelly, 10% (w/v) (Blackcurrant 25% reduced sugar, Woolworths, Australia), SAXA NaCl Salt (29% w/v) (Table salt, naturally evaporated sea salt, Woolworths, Australia) and tap water.

Edible gold leaf (12 Karat white gold, The Gold Leaf Factory, Australia) was purchased online from goldleaf.com.au.

2.1.4. Capacitive pressure sensor. Capacitive pressure sensors were constructed using food grade materials listed in section 2.1.1. Additional materials used were cling wrap (Glad, 60m BPA free), carbon fibres (Type C50T024, SGL Carbon Fibres LLC, Evanston, WY, USA) and glue (UHU, solvent free stick).

2.2. ICE Hydrogels Preparation

All ICE gels were prepared while being heated to 80 °C and stirred at 300 rpm (Stuart hotplate stirrer, CB162, Australia). 1 g gellan gum was first dissolved in Milli-Q water (100 mL, 80 °C). 1.75 g gelatin was added and followed by Ca^{2+} (2% w/w to gellan gum). Finally, genipin (25% w/w to gelatin) was added and allowed to stir for 3 minutes. Genipin forms a blue colour when a reaction occurs involving an amino acid. In this case, the genipin is cross-linking gelatin via primary amines found predominantly on the lysine residues of the protein chains. The solution was poured into a glass Petri dish (5 cm diameter) or plastic mould (Figure 2b) for compression tests and conductivity analysis, respectively. Samples were sealed and left to cure for 24 hours at 21 °C.

2.2.1. Addition of ionic charge carriers prior to gelation. ICE gels with varying concentrations of Ca^{2+} and Na^+ in place of the 2% w/w Ca^{2+} described in section 2.2 were prepared. The amounts of $CaCl_2$ and NaCl added to reach the required Ca^{2+} % w/w and Na^+ % w/w concentrations are found in Tables 1 and 2, respectively.

Table 1 Quantities of $CaCl_2.2H_2O$ added for different Ca^{2+} %w/w used in preparing ICE gels.

Ca^{2+} (%w/w)	*0.4*	*0.8*	*2*	*4*	*8*	*20*
$CaCl_2.2H_2O$ (g)	0.015	0.029	0.073	0.147	0.293	0.734

Table 2 Quantities of NaCl added for different Na^+ %w/w used in preparing ICE gels.

Na^+ (%w/w)	*25*	*50*	*70*	*80*	*100*
NaCl (g)	0.6	1.3	1.8	2	2.5

2.2.2. Addition of ionic charge carriers after gelation. Hydrogels were prepared according to section 2.2. Once set, gels were soaked in 2, 4.4 or 6.2 molar concentrations of NaCl solution for 24 hours in a sealed container.

During conductivity optimisation, ICE hydrogels were soaked in 11 molar concentrated CsCl solutions for 24 hours in a sealed container.

2.3. Edible Robust Hydrogel Electrode Preparation

3 g of food grade gelatin was dissolved in tap water (100 mL, 80 °C) under rapid stirring. 2 g of food grade alginate was added under the same conditions. The solution was poured into a glass Petri dish or plastic mould for mechanical testing and conductivity analysis. Samples were soaked in 1 M $CaCl_2$ for 1

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hour, followed by soaking in a saturated (6.2 M) solution of food grade NaCl.

2.4. Characterisation

All characterisation experiments were carried out at 21°C, 45% relative humidity, unless otherwise stated.

2.4.1. Water content. Water content (*WC*) of the hydrogels was calculated as (%w/w) using the following equation:

$$WC = \left(\frac{SH-DH}{DH}\right)x\ 100, \quad (1)$$

where the swollen (*SH*) and dry hydrogel (*DH*) indicate the weight of hydrated and dehydrated samples, respectively. The hydrogels were dried by placing them in a temperature and humidity chamber (Thermoline Scientific, Australia) at 60 °C for 24 hours under relative humidity of 45%.

2.4.2. Volume change from swelling. Volume change (*VC*) as a result of soaking hydrogels in a salt solution was measured using the following equation:

$$VC = \left(\frac{SH-RS}{RS}\right)x\ 100\ , \quad (2)$$

where the reference state (RS) refers to the gels prior to being soaked in a salt solution and swollen hydrogels (SH) refer to gels which have been soaked in a salt solution.

2.4.3. Compression testing. Compression analysis was performed using a universal mechanical testing apparatus with a 500 N load cell (EZ-S, Shimadzu, Japan). Gellan gum/gelatin ICE gel samples were cut in to cuboids (10 mm x 10 mm x 10 mm) and compressed at 1 mm/min at 21 °C, with the exception of the alginate/gelatin robust hydrogels; these were prepared using a circular die cutter to create cylinders with diameters of 15 mm and 10 mm heights. The alginate/gelatin robust hydrogels were then immersed in a 1 M $CaCl_2$ solution for 1 hour resulting in a cylinder of approximately 12 mm in diameter and 9 mm in height. The stress-strain data was used to calculate the compressive strain energy at failure (U), compressive stress at failure (σ_c), secant modulus over 20-30% strain (E_c) and compressive strain at failure (ε_c).

2.4.4. Tensile testing. Gels for tensile testing were cast in a dog bone plastic mould of 5 mm thickness, neck width of 6 mm and gauge length of 20 mm. Hydrogels were extended at 1 mm/min at 21 °C. The stress-strain data was used to calculate the work of extension (W), tensile stress at failure (σ_t), Young's modulus (E_t) and tensile strain at failure (ε_t).

2.4.5. Impedance analysis. Using a custom built instrument[35] (Figure S1) the impedance behaviour of the gel samples were obtained for frequencies between 1 Hz and 100 kHz. Reticulated vitreous carbon (RVC, ERG Aerospace, conducting carbon foam structure with 20 pores per inch) was used for gel-electrode contact. The impedance measurements were conducted on gels with cross-sectional area of 0.3 cm^2 at 5 different lengths (0.5 cm - 2.5 cm).

Impedance analysis was performed by applying 1 V (alternating signal) using a waveform generator (Agilent U2761A) across the circuit with a known resistor (R_k) and measuring the voltage drop using an oscilloscope (Agilent U2701A) across the gel sample.

Bode plots, which are standardly plotted on log-log scales, have been displayed on linear-log scales for ease of differentiation between data series. Plotting as log-log caused series to be overlapped.

Equivalent circuit modelling was performed to elucidate the impedance behaviour of hydrogel samples. Three-parameter fits of resistors, Warburg elements and capacitors in series were computationally modelled.

2.4.6. Statistical treatment of data. Findings reported are average results from triplicate experiments. Errors reported were calculated as standard deviations of the mean for each experiment. Q-tests with confidence intervals above 95% were used to identify and reject outlying data.

2.4.7. Fabrication of capacitive pressure sensor. ICE gels were prepared according to section 2.2 and cast on glass templates approximately 40 mm x 25 mm x 1.2 mm. Carbon fibres were placed within the gel prior to gelation to establish connection between the electrodes and multimeter (Figure S2). Electrodes were left to gel under ambient conditions for 1 hour at 21 °C. Once gelled, electrodes were cut into dimensions of 25 mm x 15 mm, and stored in a glass petri dish with saturated (6.2 M) NaCl solution at 21 °C for 24 hours.

The dielectric was prepared using a 10% w/w genipin to gelatin (GGN) hydrogel. These were prepared by dissolving 3 g of gelatin in 30 mL of milli-Q water at 80 °C under rapid stirring. 3 mL of 25% (w/v) genipin (in a 60% ethanol 40% milli-Q solution) was added and allowed to stir for 90 seconds. Solutions were poured in a petri dish, sealed and allowed to gel for 24 hours at 21 °C. Once set, the hydrogels were cut into strips of 20 mm x 25 mm x 2 mm for use as a dielectric layer.

The electrodes and dielectric were encapsulated using non-toxic cling wrap. Assembly of the sensor was constructed by placing the dielectric layer in between the electrodes, Figure 1 and 2f. Electrodes were constructed with an overlapping dimension of 20 mm x 15 mm. Layers were glued together.

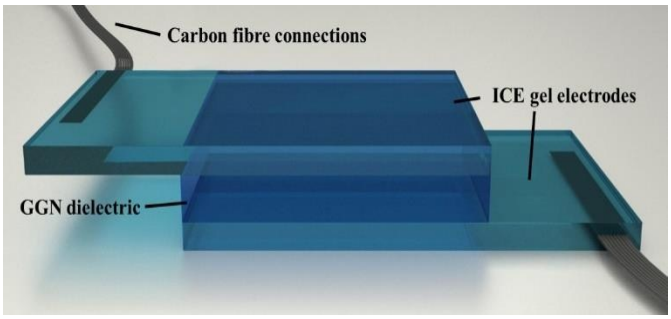

Figure 1 Schematic of capacitive pressure sensor.

2.4.8. Characterisation of edible capacitance pressure sensing device. Characterisation of the pressure sensors sensitivity was performed via measurement of the capacitance change as a result of an applied force. A digital multimeter (Keysight Agilent Technologies, 34410A) was used to record capacitance and the universal mechanical testing apparatus was used to apply a constant compressive force (Figure S2). Devices were compressed at a rate of 1 mm/min to a maximum pressure of 20 kPa and then the applied load removed at a rate of 1 mm/min. Each device had five cycles of an applied load of 20 kPa and this was repeated three times and with three different sensors. Software used to obtain mechanical and capacitive data were Trapezium and Benchvue, respectively.

3. Results and Discussion

ICE hydrogel samples were prepared using the hydrogel forming polymers gelatin and gellan gum (Figure 2a). The interaction between the ions and the polymer networks was investigated by examining the resulting effects on the mechanical and electrical characteristics of the gels.

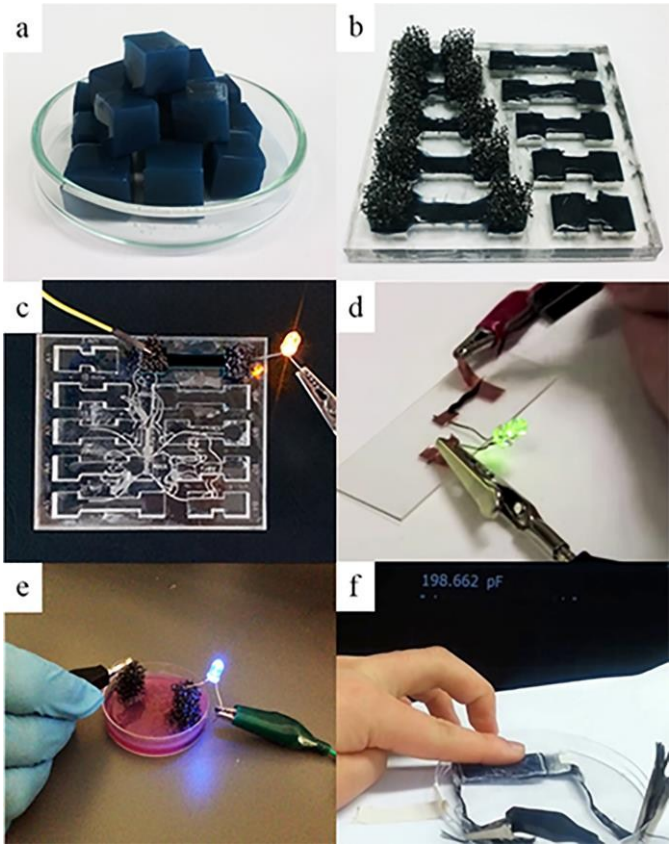

Figure 2 a) Gellan gum/gelatin ICE hydrogels cut into 10 x 10 x 10 mm^3 cubes. b) Gellan gum/gelatin ICE hydrogels in impedance moulds with (left) and without (right) RVC electrodes. c) LED illumination via conduction through an ionically (NaCl) conducting gellan gum/gelatin ICE hydrogel. d) Vegemite used to complete an electrical circuit and light an LED. e) LED illumination via conduction through an ionically (NaCl) conducting edible jelly (Blackcurrant flavouring). f) Food grade materials used to construct a capacitive pressure sensor with electrodes made using ionically (NaCl) conducting gellan gum/gelatin ICE hydrogel and a genipin-gelatin dielectric.

3.1. Electrical Characterisation

A Bode plot of the impedance magnitude as a function of frequency is plotted for each hydrogel of varying channel length (Figures 3 and 4). As the frequency is increased, there is a corresponding decrease in the impedance magnitude. This correlates to the transition of the ion mobility from long range motion to short range motion.[35] The complete switch to short range motion is indicated by the impedance becoming independent of frequency. This can be explained by the ions becoming trapped within their potential wells at high frequencies.[36] The magnitude at which the impedance becomes independent of frequency is referred to as R_I. Equivalent circuit modelling was used to determine the R_I value.

3.1.1. Modelling impedance behaviour. The frequency-dependent behaviour is suggestive of diffusion-based charge carrier mobility. As such, the hydrogel can be modelled as a complex combination of components including a Warburg diffusion element. It is proposed that the hydrogel is behaving like a Warburg diffusion element (Z_W) in series with a resistor (R_I) and capacitor (Z_C) according to the following equation:

$$|Z| = \sqrt{R_I^2} + \sqrt{Z_W^2} + \sqrt{Z_C^2}, \quad (3)$$

Z_W and Z_C may be described as:

$$Z_W = \frac{\sqrt{2}W}{\sqrt{f}}, \quad (4)$$

$$Z_C = \frac{1}{2\pi f C}, \quad (5)$$

where f is the frequency, W is the diffusion and C is the capacitance. The capacitive component of the hydrogel may be attributed to the electronic double layer which develops between the ionic charge carriers and the electrodes.[37]

The electrical impedance as a function of frequency was computationally modelled using a 3-parameter fit to equation 3, to provide values for R_I, Z_W and Z_C. Figure 3 illustrates a typical graph of experimental vs modelled data. As can be seen, the experimental data has a very close fit to the modelled data, indicating that the proposed equivalent circuit model of a capacitor, resistor and Warburg diffusion element in series can be used to study the gels ionic conductivity. Furthermore, the resistive component is representative of the impedance at high frequencies (where diffusion and capacitance are negligible) and increases with length allowing for the following equation to be applied:[35]

$$R_I = \frac{L}{\sigma A_c} + R_c, \quad (6)$$

where L is length, A_c is cross-sectional area and R_c is contact resistance. By plotting R_I as a function of the lengths of the samples, the data can be fitted to equation 6; yielding the conductivity (σ) and contact resistance (R_c) (Figure 4).[35]

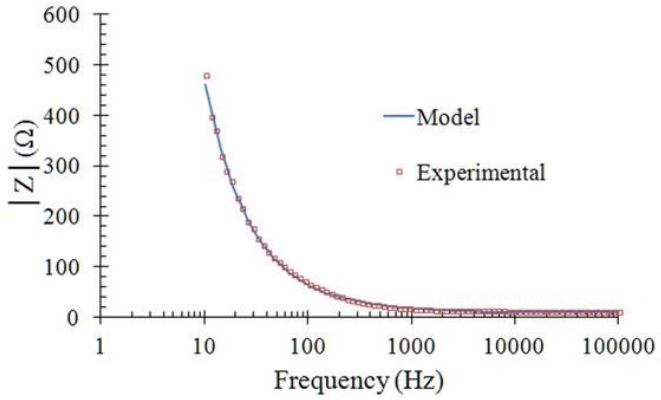

Figure 3 Frequency dependent impedance plots for a 0.5 cm gellan gum/gelatin ICE gel after 24 hours soaking in an 11 molar (saturated) concentration of CsCl solution at 21°C. Solid line represents data modelled from equation 3.

3.2. Increasing Ionic Charge Carriers

Optimisation of the ionic conductivity was sought by means of introducing large quantities of ionic charge carriers via two different methods.[36–42] Using a gellan gum/gelatin ICE gel, the addition of ionic charge carriers was explored by (i): increasing the concentrations of ionic species prior to gelation or (ii): increasing the concentrations of monovalent ions after gel formation.

3.2.1. Increasing concentrations of calcium chloride prior to gelation. $CaCl_2$ is a standard cross linker of gellan gum. The effect of increasing concentrations of Ca^{2+} cross linkers, from 0.4% to 20% w/w (to gellan gum), was investigated. The results are illustrated in Figure 5a and summarised in Table S1.

Figure 5a shows a summary of conductivity and compressive stress at failure as a function of Ca^{2+} %w/w. As can be seen, optimal compressive strength is achieved at 2% w/w Ca^{2+} to gellan gum and that increasing the concentration of ionic cross linker above this value results in a decrease in mechanical strength of the gels. Furthermore, it was observed that no significant increase in conductivity occurs for concentrations below 2% w/w Ca^{2+}.

These results indicate that up until 2% w/w Ca^{2+}, all calcium ions participate in ionic bonding of the gellan gum network. At concentrations above 2% w/w Ca^{2+} an almost linear increase in conductivity can be observed. This is thought to result from optimal crosslinking being achieved when the concentration of calcium ions reaches stoichiometric equivalence to the carboxylate groups (one Ca^{2+} for every two carboxylate groups).[20] Therefore, free ions available for conduction may only be created after all available carboxylic acid groups are crosslinked.

However, compressive stress at failure of the gels decreases with increasing concentrations of cross linker (Table S1). This behaviour has previously been attributed to calcium ions inducing molecular shielding/hindrance of the gelatin networks.[25] This shielding prohibits the formation of the covalent cross linkages in the gelatin network, resulting in reduced gel strength.

Therefore, by increasing the concentration of Ca^{2+} cross linker, an increase in the conductivity of the hydrogels can be achieved, however, this increase in conductivity corresponds with a decrease in mechanical strength of the ICE gels. Consequently, a simultaneously highly conductive and strong hydrogel cannot be achieved using this method.

To overcome the phenomenon of diminishing strength with increasing conductivity, sodium cations were explored, since monovalent salts require much larger concentrations to initiate the gelation of gellan gum.[20,43] It was proposed that increasing concentrations of sodium ions could therefore be introduced without compromising strength.

3.2.2. Increasing concentrations of sodium chloride prior to gelation. Monovalent cross linkers, such as Na^+, are known to be less effective at initiating gelation of the gellan gum network; forming a coordination complex rather than ionic bonds between carboxyl groups along the gellan gum chains.[20,43,44] This form of monovalent crosslinking can require up to 30 times the cationic concentration compared with divalent crosslinking to achieve a maximum in compressive stress at failure.[20] Therefore, monovalent ions were introduced to the ICE hydrogels during mixing to examine if an increase in the ionic conductivity of the ICE gels could be achieved without sacrificing mechanical characteristics. The results are displayed in Figure S3 and Table S2. It was found that 25% w/w Na^+ produces the strongest hydrogels and that increasing the concentration of ionic cross linker above this value resulted in a decrease in mechanical strength.

Figure S3 demonstrates that Na^+ concentrations from 25 to 70% w/w results in proportional increases in conductivity. The conductivity rapidly increases with increasing amounts of Na^+ cross linkers after 70% w/w Na^+ which corresponds with a plateau of compressive stress at failure.

By a comparison of Tables S1 and S2 it can be seen that the ICE gels made using monovalent sodium ions result in weaker gels. The resulting weaker ICE gels were unexpected, as other studies which used monovalent cations, such as potassium chloride[45], were able to produce stronger gellan gum gels when compared to crosslinking via divalent cations. This decrease in strength for monovalent crosslinked gels may be a result of the sodium coordination complexes, which form during monovalent crosslinking being less effective at dissipating loads within an ICE gel compared to divalent ionic bonding. In addition to this, a conductivity of greater than 100 mS/cm could not be achieved without sacrificing considerable hydrogel strength.

It was observed that greater quantities of sodium ions, compared to calcium ions, could be used to crosslink the gellan gum/gelatin ICE gels without such drastic reductions in mechanical properties. This was seen that ICE gels crosslinked with Na+ had a change of maximum compressive stress from 0.5 ± 0.1 MPa to 0.27 ± 0.02 MPa when the crosslinking concentration increased from 25% w/w to 50% w/w. In contrast, ICE gels crosslinked with $Ca2^+$ had a change in maximum compressive stress of 1.0 ± 0.2 MPa to 0.5 ± 0.1 MPa when the crosslinking concentration was increased from 2% w/w to 8% w/w. Hydrogels which were crosslinked with Na^+ could be produced with a compressive strength of 0.5 ± 0.1 MPa and a conductivity of roughly 10 ± 1 mS/cm, while a Ca^{2+} crosslinked ICE gel with equivalent strength had a conductivity of roughly 4.4 ± 0.6 mS/cm.

Consequently, as with Ca^{2+} the conductivity of the Na^+ crosslinked ICE gels was enhanced with increasing amounts of salt added, but were accompanied with a reduction in gel strength. Therefore, to overcome this addition of ions post gelation of gellan gum/gelatin ICE gels with 2% w/w Ca^{2+} was investigated.

3.3. Post-gelation Ion Addition

The introduction of ions during gelation was found to interrupt the formation of covalent bonding between carboxylate groups along the gelatin network. This was thought to be a result of the excess ions

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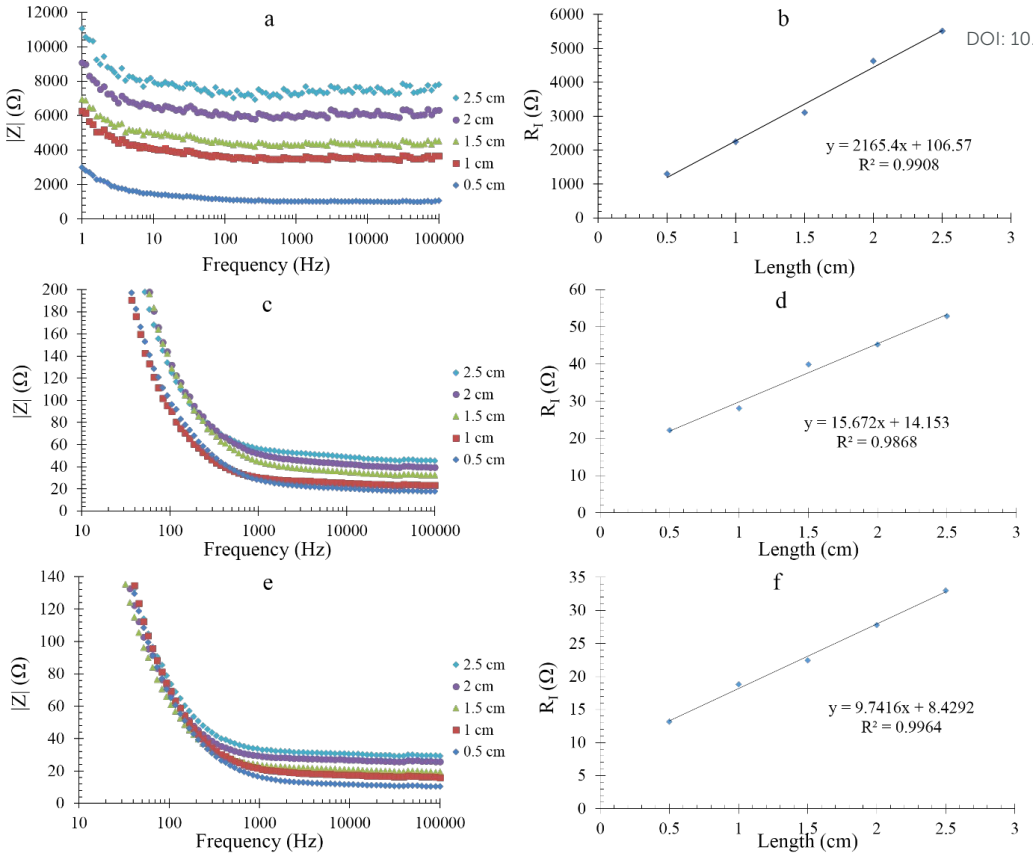

Figure 4 Typical Bode plots of gellan gum/gelatin ICE gels a) crosslinked with 2% (w/w) Ca^{2+} as-prepared, c) soaked in a c) 6.2 M NaCl solution and e) an 11 M CsCl solution at 21°C. Samples of gellan gum/gelatin ICE gel resistances as a function of gel length b) as-prepared, d) soaked in a 6.2 M NaCl solution and e) soaked in an 11 M CsCl solution at 21°C. Trend lines in b), d) and f) are fits to equation 4.

molecular shielding/hindrance of the carboxylate charges, preventing the genipin from initiating nucleophilic substitution.

Therefore, an examination of the interactions between the excess ionic species and gellan gum/gelatin ICE gels after gelation was performed to circumvent this phenomenon.

3.3.1. ICE gel soaked in sodium chloride post gelation. The gellan gum/gelatin ICE gels were prepared as described in section 2.2.2 using Ca^{2+} (2% w/w to gellan gum) and genipin (25% w/w to gelatin). After gelation, the hydrogels were soaked in various concentrations of NaCl for 24 hours, with the effect on the mechanical and conductive properties shown in Figure 5b and summarised in Tables 3 and 4.

It was seen that the introduction of NaCl ions had no adverse effect on the mechanical properties of the gel. This is a dramatic improvement compared to ICE gels which had ions added prior to gelation. ICE gels soaked in a 6.2 molar (saturated) concentration of NaCl solution, exhibited a maximum compressive stress of 1.4 ± 0.2 MPa and compressive strain of 91% ± 3% (Table 3). The ICE gels increase in mechanical performance may be attributed to the excess ions causing charge shielding of the functional groups along the polymer chains. This shielding of the charged functional groups reduces the repulsive forces between chains and results in increased chain associations and stronger gels. However, there was a reduction of the secant modulus when salt was added to the polymers. This indicates a reduction of the gels stiffness. Similarly, the decrease in stiffness of the polymer may also be due to the charge shielding of the functional groups allowing the chains to be compressed together with less resistance.

The results from figures 5b and table 4 demonstrate that increasing concentrations of NaCl led to an increased ionic conductivity of the hydrogels, i.e. 200 ± 20 mS/cm when soaked in ~6.2 molar (saturated) NaCl. This is considerably higher compared to the conductivities of ICE hydrogels prepared with addition of ions prior to gelation. It should be noted that these gels had a water content of 81% ± 1% (w/w). The conductivity observed for these ion soaked ICE hydrogels was the highest amongst conductive hydrogels in the literature with water contents above 80 % w/w, to the best of our knowledge.

Using the modelling described in section 3.1.1 the Warburg element was found to decrease from 2500 ± 300 $\Omega/s^{1/2}$ to 440 ± 40 $\Omega/s^{1/2}$ when modelling as prepared gels and gels soaked in a 6.2 M NaCl solution, respectively. This indicates that as the conductivity of a gel increases due to the increased concentration of salt, the Warburg element decreases. Furthermore, it was observed that the capacitance of the gels increases as a result of using higher concentrations of NaCl. This is to be expected when adding increasing amounts of charge carriers to the system. However, for the as prepared gels the capacitance was too low to be modelled using equation 3 so was considered to be negligible; ICE gels soaked

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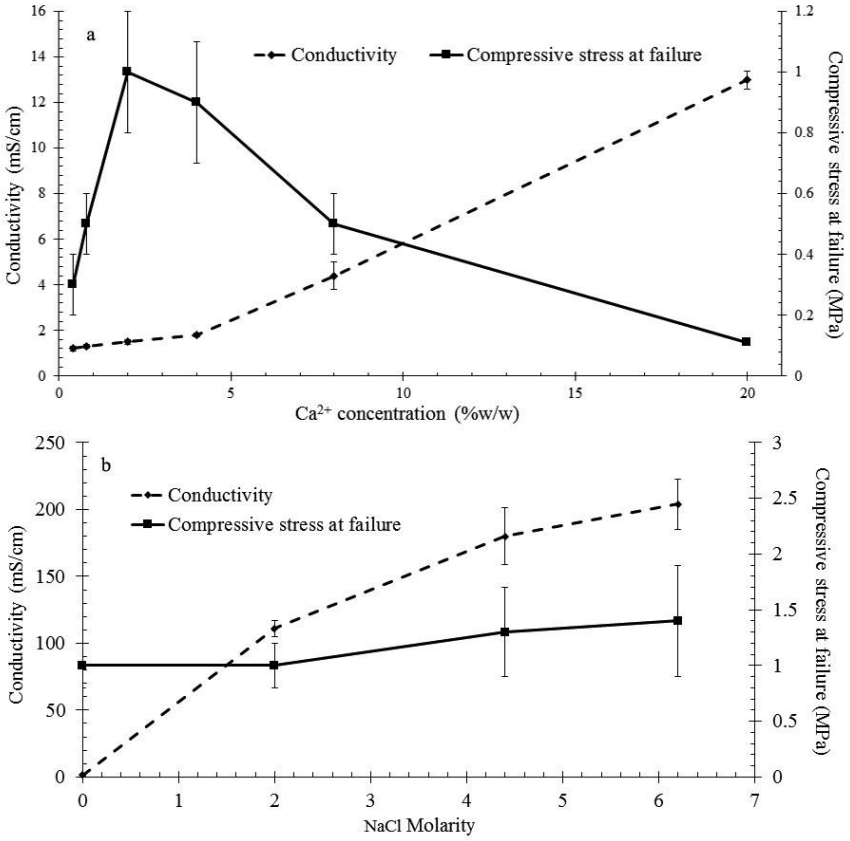

Figure 5 a) Summary of conductivity (blue) and compressive stress (red) at failure as a function of Ca^{2+} cross linker concentration of different ICE gels at 21°C. b) Summary of compressive stress at failure and conductivity as a function of NaCl solution molarity in which the ICE gels prepared with 2% w/w Ca^{2+} (to gellan gum) and 25% w/w genipin (to gelatin) were soaked for 24 hours at 21°C. Solid lines are a guide for the reader's eye.

in a 2 M NaCl solution displayed an unusually high capacitance. This high capacitance was thought to be a result of the limitation of the software.

These results indicate that soaking hydrogels in a salt (NaCl) solution can be used as an easy method to create highly conductive gels without sacrificing mechanical characteristics.

3.4. Optimisation of Conductivity

Means of optimising the system for enhanced electrical properties were explored by altering the type of ionic charge carrier used for conduction within the gellan gum/gelatin ICE gels.

3.4.1. Caesium chloride. Ion mobility is strongly related to Stokes radius of a molecule, whereby a small Stokes radius results in high ion mobility.[46] Large monovalent ions have a small Stokes radius. Subsequently, caesium is the largest of the alkali metals (excluding radioactive francium) and therefore should have the lowest Stokes radius (and highest mobility) out of all monovalent cations.[47] Furthermore, the solubility of alkali metal salts increases as the cation lies further down the periodic table. Therefore, as caesium chloride has a very high solubility and mobility it was used to optimise the electrical characteristics of the hydrogel. Results are summarised in Table 3 and 4.

ICE gels soaked in an 11 molar (saturated) concentration of CsCl solution exhibited a maximum compressive stress of 1.5 ± 0.4 MPa and compressive strain of 91% ± 2%. There was also a distinct reduction in the stiffness of the gels. The effects of inclusion of CsCl into the ICE gel mirror those observed using NaCl. This may once again be attributed to charge shielding of function groups by the added salt. Therefore, from these results and those presented in section 3.3, it can be seen that the reduction of stiffness of the hydrogels and enhanced mechanical performance are not unique to the type of salt used to submerge the gels, but are commonly observed when excess ions are introduced into ICE hydrogels post gelation.

From the results shown in Table 4, by soaking ICE gels in approximately 11 molar (saturated) concentrated caesium chloride solution hydrogels were produced with a conductivity of 380 ± 30 mS/cm and a water content of 36% ± 1% (w/w). The water content appears to drastically reduce, from 97.5% to 36% when compared to as prepared gels. However, this is largely a result of the addition of large quantities of CsCl salt reducing the mass fraction of the water rather than a consequence of dehydration of the gels. This can be seen in table 3 whereby a reduction in water content via addition of salt did not result in a loss of mechanical properties and no observable change in the swelling volume of the gels after soaking in a salt solution.

Furthermore, the additions of large quantities of CsCl were also shown to reduce the Warburg element of the gels for as prepared gels and CsCl soaked gels, respectively. In addition to this, the capacitance was shown to drastically increase for the CsCl soaked ICE gels. These results reflect the trend whereby use of salt increases the

conductivity of the gels, reduces the Warburg element and raises the capacitance, as was seen when using NaCl.

This further highlights this method as a means of inducing high conduction within hydrogels without sacrificing mechanical properties.

3.5. Edible Robust Hydrogel Electrodes

Using the premise that ionic species can be used to create highly conductive hydrogels the construction of simple, highly conductive, robust electrodes made from food grade products purchased from supermarkets and online gourmet shops was explored. A highly conductive hydrogel electrode was produced using a hybrid gel of alginate and gelatin (Alg-Gel) crosslinked by soaking for 1 hour in a 1 M $CaCl_2$ solution. This was followed by immersing the gel in a saturated (6.2 M) table salt (NaCl) solution for 24 hours. The mechanical and electrical properties of this hydrogel were examined with the results shown in tables 3, 4 and 5.

The hydrogel exhibited a conductivity of 190 ± 20 mS/cm, a compressive stress at failure of 2.2 ± 0.2 MPa and a water content of 62% ± 3% (w/v). Tensile testing of the gels revealed a maximum tensile strength of 62 ± 17 kPa and a strain of 98% ± 28%, respectively. These findings demonstrate the creation of a conductive and robust hydrogel system from food grade materials which can be used for the advancement of edible devices.

Table 3 Mechanical properties of hydrogels after 24 hours' immersion in different concentrations of salt solution. ICE-Ca^{2+} are gellan gum/gelatin ICE gels containing 2% Ca^{2+} (w/w) and Alg-Gel are robust hydrogel electrodes made from food grade alginate and gelatin. σ_c, ε_c, E_c, U and σ indicate compressive stress at failure, compressive strain, secant modulus (20-30%) and strain energy to failure, respectively.

Gel	*Soaking*	*Molarity*	σ_c *(MPa)*	ε_c *(%)*	E_c *(MPa)*	*U (kJ/m³)*
ICE-Ca^{2+}	-	-	1.0 ± 0.2	84 ± 3	0.15 ± 0.05	130 ± 30
ICE-Ca^{2+}	NaCl	2 M	1.0 ± 0.2	84 ± 3	0.13 ± 0.01	140 ± 30
ICE-Ca^{2+}	NaCl	4.4 M	1.3 ± 0.2	88 ± 3	0.09 ± 0.04	160 ± 30
ICE-Ca^{2+}	NaCl	6.2 M	1.4 ± 0.2	91 ± 3	0.07 ± 0.02	150 ± 40
ICE-Ca^{2+}	CsCl	11 M	1.5 ± 0.4	91 ± 2	0.06 ± 0.02	150 ± 20
Alg-Gel	NaCl (table salt)	6.2 M	2.2 ± 0.2	83 ± 6	0.26 ± 0.07	310 ± 25

Table 4 Electrical properties of hydrogels after 24 hours' immersion in different concentrations of salt solution. ICE-Ca^{2+} are gellan gum/gelatin ICE gels containing 2% Ca^{2+} (w/w) and Alg-Gel are robust hydrogel electrodes made from food grade alginate and gelatin. σ, μ_w and C indicate conductivity, Warburg coefficient and capacitance, respectively.

Gel	*Soaking*	*Molarity*	σ *(mS/cm)*	μ_w *(Ω/s$^{1/2}$)*	*C (μF)*	*Water Content (%)*
ICE-Ca^{2+}	-	-	1.5 ± 0.1	2500 ± 300	-	98 ± 1
ICE-Ca^{2+}	NaCl	2 M	110 ± 10	530 ± 10	28 ± 6	89.9 ± 0.1
ICE-Ca^{2+}	NaCl	4.4 M	180 ± 30	490 ± 10	21 ± 1	83.3 ± 0.9
ICE-Ca^{2+}	NaCl	6.2 M	200 ± 20	440 ± 40	24 ± 4	81 ± 1
ICE-Ca^{2+}	CsCl	11 M	380 ± 30	350 ± 20	41 ± 5	36 ± 1
Alg-Gel	NaCl (table salt)	6.2 M	190 ± 20	550 ± 20	50 ± 3	62 ± 3

Table 5 Mechanical properties of Alg-Gel hydrogel electrodes under tension after immersing gels in a saturated (6.2M) table salt solution for 24 hours. σ_t, ε_t, E_t and W indicate tensile stress at failure, tensile strain, Young's modulus and work of extension, respectively.

σ_t *(kPa)*	ε_t *(%)*	E_t *(kPa)*	*W (kJ/m³)*
62 ± 17	98 ± 28	72 ± 4	34 ± 10

3.6. Conductive Patterns from Commercially Available Edible Products

To assess the potential of common food products to assist in the creation of edible electronics, two edible spreads already containing salt (Vegemite and Marmite) and an edible jelly (Aeroplane Jelly) with added table salt were investigated.

Vegemite and Marmite are common condiments which contain large quantities of salt. These products were studied to evaluate their capacity to act as conductive connections in edible devices. The results are displayed in table 6. It was found that both these products are inherently conductive displaying conductivities of 20 ± 3 mS/cm and 13 ± 1 mS/cm for Vegemite and Marmite respectively. The conductivity of these condiments is a result of the salt contained with them as Vegemite has a sodium content of 3.45% (w/w)[48] and Marmites contains a sodium and potassium content of 3.31% (w/w) and 2.86% (w/w), respectively.[49] However, although Marmite appears to have a higher quantity of salt, Vegemite displays superior conductivity. This is most likely a result of the higher water content within Vegemite (33%) compared to Marmite (29%) resulting in a higher conductivity as, according to the temperature-frequency-moisture superposition principle, an increase in the hydration of the gels is akin to an increase in temperature leading to higher conductivities within ionic conductors.[36,40,41]

Modelling of the impedance behaviour demonstrated that the capacitance for Vegemite and Marmite was also shown to be similar. Vegemite was shown to have a higher conductivity than Marmite, however the Warburg element for Vegemite was higher and the capacitance lower than Marmite. This indicates that the Warburg

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element and capacitance of the conductors is strongly related to the concentration of salt in the gels rather than the overall conductivity.

Furthermore, the edible gelatin product aeroplane jelly was explored to observe if it could be constructed into conductive materials via the inclusion of table salt during preparation. It was shown that the resulting materials using a one-pot synthesis method with jelly, displayed a conductivity of 150 ± 20 mS/cm at a water content of 70% ± 2%.

Finally, electronically conductive edible gold leaf was analysed to observe its potential for the construction of edible electrodes. It was found to display a conductivity of $3.8 \times 10^8 \pm 5.0 \times 10^7$ mS/cm.

Table 6 Electrical properties and water contents of Food products Vegemite, Marmite and Jelly with table salt. σ, μ_w and C indicate conductivity, Warburg element and capacitance, respectively.

Material	*σ (mS/cm)*	*μ_w ($\Omega/s^{1/2}$)*	*C (μF)*	*Water Content (%)*
Vegemite	20 ± 3	2280 ± 90	14 ± 1	33 ± 1
Marmite	13 ± 1	1900 ± 200	18 ± 5	29 ± 1
Jelly	150 ± 20	550 ± 70	58 ± 8	70 ± 2
Gold Leaf	$3.8 \times 10^8 \pm 5.0 \times 10^7$	N/A	N/A	N/A

3.7. Capacitive Pressure Sensor

Recently, a hydrogel based capacitive pressure sensor was demonstrated by Sun. et. al. (2014) in their replication of human skin.[50] Inspired by this work a hydrogel capacitive pressure sensor was made using our edible materials.

3.7.1. Device characterisation. A capacitive pressure sensor containing edible components, i.e. NaCl soaked gellan gum/gelatin ICE gels as electrodes and a 10% (w/w) genipin-gelatin dielectric (Figure S2), was constructed. The limit of detection (LOD) of the device was determined to be 7 ± 2 pF, which corresponds to a pressure of 1.3 ± 0.4 kPa (see supplementary information).[51]

The devices performance was determined by subjecting the sensor to 5 cycles of 0-20 kPa (Figure 6c). The sensor showed a linear capacitive response to the applied load from 4-20 kPa (Figure 6a). The non-linear response within the region of 0-4 kPa was resolved to be a result of connection between the electrodes and dielectric being established. The average response of the device using 3 repeats of 5 cycles was determined to be 0.80 ± 0.06 pF/kPa. This response was found to be more sensitive than the hydrogel capacitive pressure sensor developed by Sun. et. al. (2014) (0.1 pF/kPa).[50] The measured response range is well within the pressures found in the stomach which can reach from 0.7 to 6.3 kPa.[52]

Furthermore, figures 6b and 6c indicate that the device was not damaged after 5 successive loadings, displaying repeatable sensitivity of 0.80 ± 0.06 pF/kPa for each of the 5 loading cycles, indicating full self-recovery. However, self- recovery was not instantaneous, as shown in figure 6c, but returned to its rest capacitance after a recovery time of 110 ± 10 s.

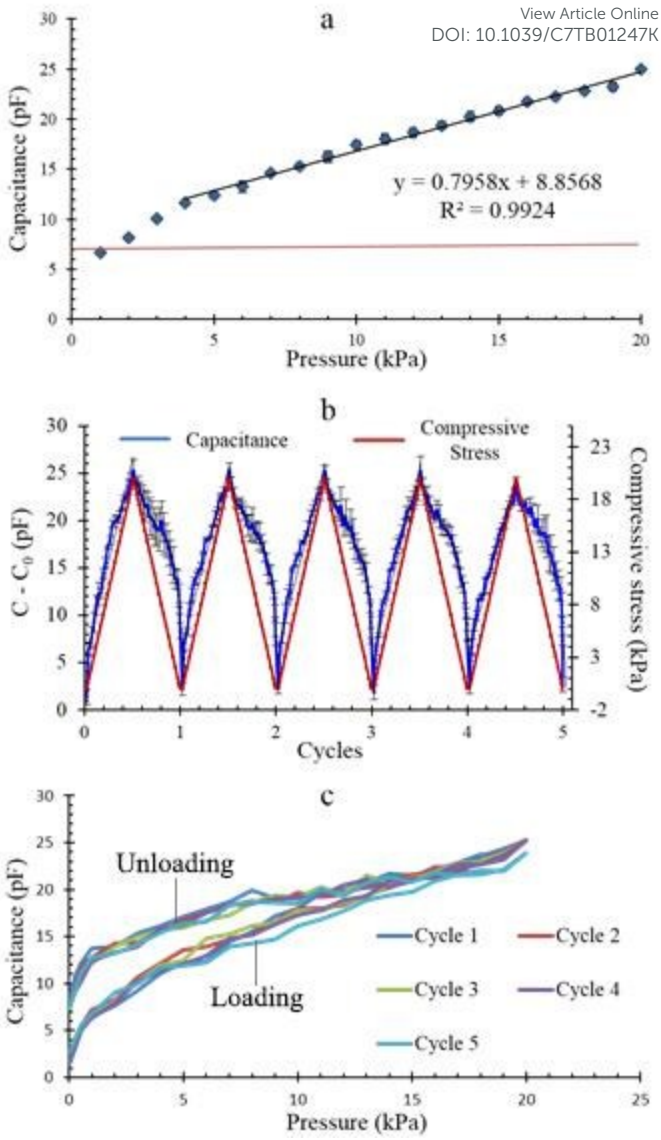

Figure 6 a) Measured capacitance–pressure curve with red line representing LOD, solid line is a linear fit to data between 4 kPa and 20 kPa of applied pressure. b) Pressure and capacitance of the edible sensor cyclically compressed to a load of 20 kPa. c) Pressure–capacitance curves for 5 cycles.

4. Conclusions

Edible devices offer physicians and researchers new opportunities to develop medical instruments for monitoring and treating the GI tract without risk of retention. Materials that are mechanically robust, electrically conductive and digestible are essential to further this field of research. During this study, food grade hydrogel materials were explored to optimise their mechanical and electrical properties for applications as components in edible devices.

It was found that the modification of hydrogels via the inclusion of ionic species resulted in large increases in conductivity without sacrificing mechanical characteristics. ICE hydrogels made of gelatin and gellan gum containing either NaCl or CsCl conductive species exhibited conductivities of 200 ± 20 mS/cm and 380 ± 20 mS/cm, respectively.

We demonstrated that hydrogel electrodes could be achieved using table salt and food grade versions of gelatin and

alginate. The resulting electrodes from these edible supermarket products exhibited a conductivity of 190 ± 20 mS/cm and compressive stress at failure of 2.2 ± 0.2 MPa. In addition, the common breakfast spreads Vegemite and Marmite displayed conductivities of 20 ± 3 mS/cm and 13 ± 1 mS/cm, respectively. This highlights the potential for edible materials sourced from supermarkets for use in fabrication of electrodes.

Lastly, we demonstrated the potential of our gel materials for device fabrication via construction of a capacitive pressure sensor using food grade components. The sensor exhibited complete self-recovery after 5 loading cycles of 20 kPa giving a repeatable sensitivity of 0.80 ± 0.06 pF/kPa, which is the most sensitive hydrogel capacitive pressure sensor in the literature, to the best of our knowledge. Devices based on these materials have the potential to be used to monitor and treat digestive pressure abnormalities such as intestinal motility disorders.

This work highlights the promise of constructing simple edible devices using common everyday salts and robust hydrogel polymers.

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